On the Electronic Structure of Highly Porous Hydrated Ruthenium Dioxide Nanomaterials

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INTRODUCTION

Nanomaterials, the materials of the 21st century, are under close scrutiny both for fundamental and technological applications such as for instance microelectronics, chemical, gas and biosensors as well as novel catalytic and photovoltaic devices.
Ruthenium dioxide is a well-known metallic oxide used as resistors, electrochemical capacitors as well as catalysts. However, the high effective cost of the ruthenium devices has contributed to a decrease in its material research activity. Nevertheless, many applications still require the very good thermal and chemical stability as well as a very low resistivity such as, for instance, the electrocatalytic process for the industrial production of oxygen and chlorine. Therefore, designing novel RuO_2 nanostructured materials may considerably reduce the cost and increase significantly the efficiency of the devices by increasing substantially the specific surface area.

BACKGROUND

The design and modeling of purpose-built metal oxide nanomaterials is achieved by following a novel concept (and experimental method) developed by Vayssieres et al [1] which takes into account the variation of the interfacial tension in the nucleation and growth process of metal oxides from aqueous solution. By chemical and electrostatic minimization of the interfacial tension of the system, colloidal thermodynamic stability may be reached yielding to well-defined and well-controlled metal oxide nanoparticles [2] as well as well-designed nanostructured thin films [3]. The control of the nanoparticle size, orientation and morphology is therefore reachable, allowing the design of a new generation of smart metal oxide nanomaterials, built for the purpose of their application. Such concept has been successfully applied in the field of electrochromic and photoelectrochemical devices [4].

EXPERIMENTAL

The samples characterization was performed by field emission scanning electron microscopy (FEG-SEM) as well as transmission electron microscopy (HRTEM) and its electronic structure investigated by x-ray spectroscopy at synchrotron radiation facility.
The soft x-ray absorption experiments (XAS) were carried out on hydrated nanostructured thin films (RuO_2.xH_2O/Ru/Teflon) and RuO_2.xH_2O powders prepared according to reference [5] as well as on commercial hydrous and anhydrous powders of RuO_2 (Aldrich). The XAS experiments were performed at beamline 7.0.1 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. The beamline comprises a 99-pole, 5 cm period undulator and a spherical-grating monochromator covering the spectral energy range between 60-1300 eV [6]. XAS spectra were recorded in two different detection mode: measuring the total electron yield (TEY) from the sample current and measuring the x-ray fluorescence yield (FY). The resolution of the monochromator was set to 0.2 eV for the O 1s absorption edge. The XAS spectra were normalized by means of the photocurrent from a clean gold mesh in front of the sample to correct for intensity fluctuations in the photon beam.

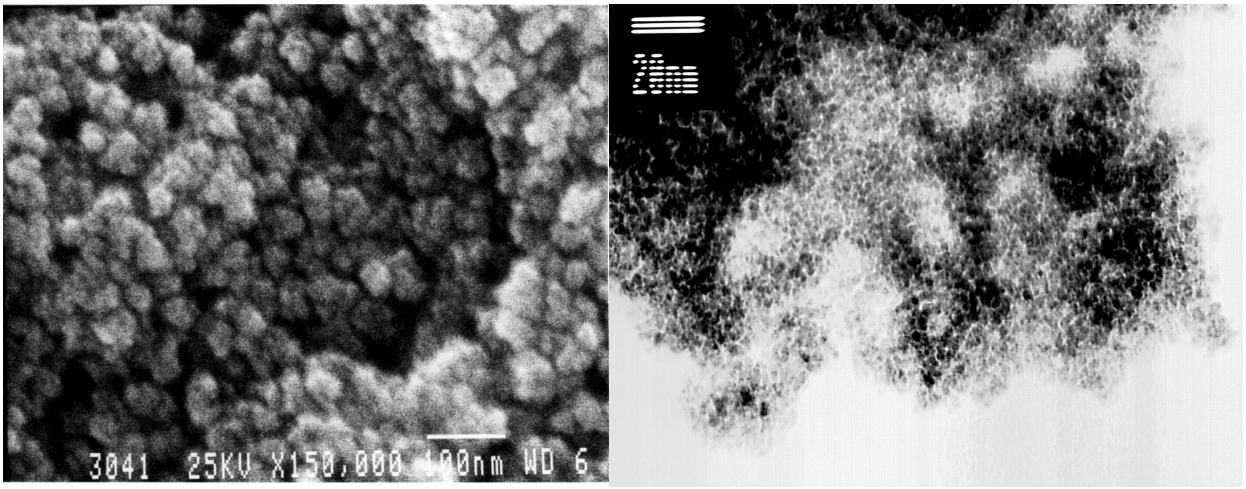

Figure 1. FEG-SEM micrograph of highly porous hydrated ruthenium dioxide thin film (left) and TEM of aqueous solution of hydrated ruthenium dioxide (right).

RESULTS ANS DISCUSSION

Figure 1 shows the micro/nano-structure of the amorphous hydrated thin film of RuO_2. The micrograph clearly indicates a very high porosity throughout the materials as well as a connected path. The individual nanoparticles of about 1-2 nm in diameter are aggregated as 10-20 nm objects in the thin film materials and accordingly, a very high specific surface area is obtained.
XAS spectra were recorded on various samples (figure 2). As reference samples, high purity hydrous and anhydrous commercial powders were used. The O 1s absorption spectrum of anhydrous powder shows the typical two-region spectrum of the transition metal oxides [7]. The first region (below the ionization threshold) is attributed to O 2p, weight-hybridized in states of predominantly metal d character, i.e. Ru 4d. The second region, above the threshold is attributed to oxygen 2p orbitals hybridized with metal *n*s and *n*p character, i.e. Ru 5s and 5p. A very high density of unoccupied states is present for anhydrous samples. On the other hand, the hydrated commercial sample shows much less resolved peak and much fewer empty states below the threshold, independently of the normalization procedure. This is understood by the presence of electronic donor levels due to hydrogenated species, such as hydroxyl groups and water molecules.

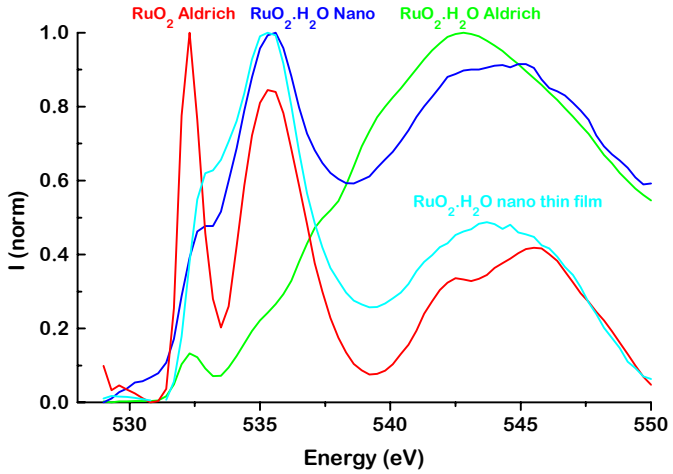

Figure 2. O1s absorption spectra (TEY mode) of various ruthenium dioxide materials.

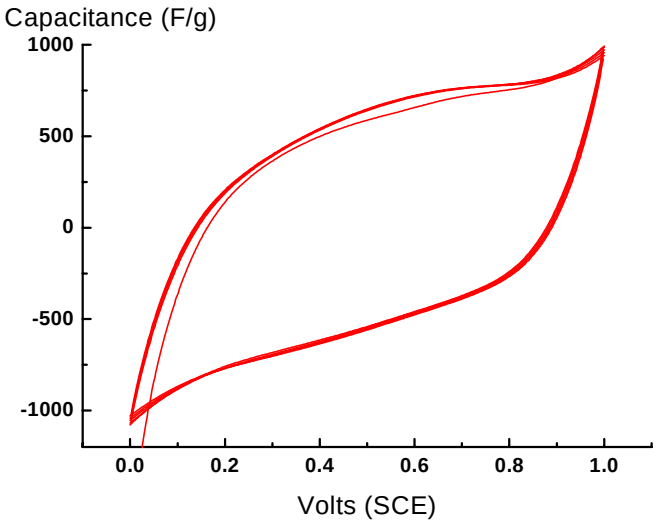

Figure 3. Cyclic voltammogram of highly porous hydrated ruthenium nanostructured thin film deposited on Teflon FEP in aqueous sulfuric acid (1M) solution (20 scans at 20mV/s).

The hydrated nanomaterials (thin films and powders), although synthesized in aqueous solution, seem to exhibit a much higher density of unoccupied states and consequently, a much lower amount of water and hydroxyl than the hydrous commercial sample. Therefore, one may take advantage of their very high surface area, the excellent chemical stability of the ruthenium dioxide materials to create nanostructured ruthenium dioxide supercapacitors. Indeed, a very high capacitance (up to 1000F/g) as well as a very good cycling capacity in acidic medium (sulfuric acid 1M) and an excellent stability are obtained. The voltammograms are feature-less for all scan rate between 2mV/s and up to 100mV/s which indicates a pure double layer capacitance.
Such nanomaterials is expected to contribute to the development of a new generation of novel and more efficient supercapacitors as well as better electrocatalysts for chlorine and oxygen evolution.

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